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Vapor-Phase Cracking and Wet Oxidation as Potential Pollutant Control Techniques for Coal Gasification

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

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Research Triangle Park, NC

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VAPOR-PHASE CRACKING AND WET OXIDATION AS POTENTIAL POLLUTANT CONTROL TECHNIQUES FOR COAL GASIFICATION

by

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16. ABSTRACT The report gives results of an investigation of two techniques (hydrocracking of heavy organics in the raw gas prior to quench, and wet oxidation of the gasifier condensate) for pollutant control in coal gasification processes. Bench-scale experiments were used to determine rates of hydrocracking and wet oxidation as a function of process conditions and catalyst used. A microreactor system, capable of holding 1.0 cc of material to be screened for catalytic activity, was used in the hydrocracking studies. Benzene and alkylated benzene compounds were used as model compounds in determining the potential of various materials for cracking rates. Thiophene was used as a model compound for catalyst poisoning studies. Cracking rates were determined for coal-derived materials produced from bituminous and subbituminous coals and materials containing iron and nickel compounds. Experiments were carried out at 300 to 800 C and approximately atmospheric pressure. The most promising material screened was a triply-promoted iron oxide ammonia synthesis catalyst. It had the greatest activity at temperatures of practical interest for a control device and showed more sulfur resistance than the other materials screened. However, the catalyst was poisoned by sulfur: attempts to regenerate it by air oxidation were unsuccessful. Wet oxidation appeared competitive.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Coal Gasification	Stationary Sources	13H
Vapor Phases	Vapor-phase Cracking	07D
Catalytic Cracking	Hydrocracking	07A
Oxidation	Wet Oxidation	07B,07C
Organic Compounds		
Condensates		
Catalysis		

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ABSTRACT

This research program was initiated with the overall objective of investigating the suitability of two techniques for pollutant control in coal gasification processes. These techniques are hydrocracking of heavy organics in the raw gas prior to quench and wet oxidation of the gasifier condensate.

Experiments were carried out in bench-scale equipment to determine rates of hydrocracking and wet oxidation as a function of process conditions and catalyst used. A microreactor system, capable of holding 1.0 cm^3 of material to be screened for catalytic activity, was used to perform the hydrocracking studies. Benzene and alkylated benzene compounds were used as model compounds in determining the potential of various materials as cracking catalysts. Thiophene was used as a model compound for catalyst poisoning studies. Cracking rates were determined for materials produced from bituminous and subbituminous coals and materials containing iron and nickel compounds. Experiments were carried out at 300° to 800°C and approximately atmospheric pressure. It was found that the most promising material screened was a triply-promoted iron oxide ammonia synthesis catalyst. It had the greatest activity at temperatures of practical interest for a control device and showed more sulfur resistance than the other materials screened. However, the catalyst was poisoned by sulfur, and attempts to regenerate it by air oxidation were not successful.

Wet oxidation experiments were carried out in a 1-liter autoclave system using gasifier quench water and a 10,000 ppm phenol solution at 150° to 200°C. In several of the experiments, gasifier char was added to the autoclave system. It was found that no measurable oxidation took place at 150°C. However, at 200°C substantial oxidation occurred. Coal char was found to approximately double the rate of wet oxidation in the phenol solution but had no apparent effect on the rate of oxidation of components in the gasifier quench water. The rates of oxidation measured in the experiments were found to be in the range which would make wet oxidation of gasifier condensate competitive with other control techniques.

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SECTION 1

INTRODUCTION

In coal gasification systems where the blast-coal contacting is countercurrent in nature, high loadings of undesirable, heavy organic compounds in the raw gas from the gasifier are common. Typically the raw gas is quenched, giving rise to an aqueous condensate stream which is characterized by a heavy organic loading and, in some instances, may contain emulsified tars and oils. Treatment of the aqueous condensate for reuse in the gasification process presents expensive and formidable problems to the widespread commercialization of coal gasification processes. For example, the cost of the equipment necessary for treatment of the condensate in a Lurgi high-Btu gasification plant represents a minimum of 8 percent of the total capital investment, according to estimates of C. F. Braun.[1]

The processing steps used in condensate treatment include solvent extraction, biological oxidation, and adsorption. However, temperature and pressure conditions of the raw gas and condensate make two other processes look technically attractive for control of undesirable components. These processes are (1) vapor phase cracking of undesirable components prior to quenching the raw gas, and (2) wet oxidation of the condensate.

Vapor phase cracking could be carried out by placing a catalytic reactor between the gasifier and the quench system. However, an appropriate catalyst must be found that can withstand the severe conditions and poisons to which the catalyst would be subjected. Also, to be economically feasible, the cracking would have to take place at temperatures close to the outlet gas temperatures of the gasifier, or about 400° to 500°C. A successful vapor phase cracking process would have advantages over the traditional quench-then-treatment approach since eliminating heavy organics from the raw gas at high temperature would reduce operational problems downstream of the gasifier, permit the recovery of high quality waste heat, and reduce the cost of condensate cleanup for reuse in the gasification process.

The other approach, wet oxidation, is a process in which dissolved or suspended organic material is oxidized in the liquid phase at an elevated temperature and partial pressure of oxygen. It is currently used as an industrial waste treatment method in a number of installations around the world. In gasification processes which utilize a shift-converter, the desirable level of steam in the feed to the shift converter is on the order of 40 percent. In order to maintain this level, the quench system must be operated at 210° to 230°C and 600 to 1000 psig. These are ideal conditions at which to feed oxygen into the condensate and carry out wet oxidation of the organic material.

To investigate these control techniques, the Research Triangle Institute (RTI) has been carrying out an experimental program. Cracking studies were performed in small bench-scale equipment (microreactors). Based on previous studies in the literature, model aromatic and sulfur-containing compounds were selected and cracked over coal-derived materials, various metals, and commercial catalysts. In the wet oxidation experiments, phenol in water solutions and coal gasifier quench waters were oxidized in the presence of coal-derived materials. This report presents the results of these studies.

SECTION 2

CONCLUSIONS

The results of the experimental studies on the cracking of selected aromatic compounds over coal-derived materials show that these materials can increase the rate of cracking of the aromatics by three orders of magnitude over the homogeneous vapor phase rate. Gasification char produced from a subbituminous coal showed a greater enhancement of cracking rates than chars produced from bituminous coals.

Several iron- and nickel-containing materials were evaluated for activity toward enhancing hydrocracking of benzene (the most stable ring compound). It was found that an iron-oxide-based ammonia synthesis catalyst completely hydrocracked benzene to methane at temperatures near 450°C, which is a temperature of practical interest for the Lurgi gasifier. However, the iron catalyst was found to be poisoned by sulfur compounds. Based on work at the U.S. Department of Energy's Morgantown Energy Technology Center on hot gas cleanup (sulfur removal) with iron oxide, regeneration of the poisoned iron oxide catalyst may be possible. However, attempts made at RTI to regenerate the catalyst were unsuccessful.

The results from the experimental studies on wet oxidation of phenol-water solutions and gasifier quench waters showed that practical oxidation rates were obtainable. The presence of coal char in the wet oxidation system appeared to approximately double the rate of oxidation of the phenol, but had no effect on the rate of oxidation of the organic constituents in the gasifier quench water.

Based on the experimental studies, both vapor phase cracking of heavy organics and wet oxidation of quench water appeared to have technical promise as control technologies in coal gasification processes. However, more information is needed in order to fully evaluate the technical and economic potential of the two control techniques.

SECTION 3

RECOMMENDATIONS

Preliminary experimental results obtained on the cracking activity of an iron oxide catalyst have shown it to be a promising hydrocracking catalyst in applications of controlling heavy organics in gasifier effluents. Catalysts composed of iron oxide are known to be regenerable from sulfur poisoning. Further work needs to be done in order to properly evaluate activation and regeneration steps for the catalyst and to investigate the effect of gas composition, pressure, temperature, and space velocity on the conversion of heavy organics in the presence of iron oxide catalysts. Based on this information, actual tests in a coal gasification system should be planned and carried out in order to demonstrate the feasibility of cracking heavy tars in coal gasifier product gases. A preliminary economic analysis of vapor phase cracking of undesirable components produced during coal gasification should be performed to establish the commercial potential of the control technique.

The work performed on wet oxidation of gasifier condensate and the use of coal char as an oxidation catalyst was a preliminary study and not planned to be exhaustive. Future work is needed so that a thorough technical and economic evaluation can be made of wet oxidation as a gasifier condensate cleanup process. Experiments should be performed using (1) a wider and higher temperature range, (2) a range of oxygen partial pressures, (3) gasifier condensates with a wider range of CODs than used in this work, and (4) a variety of catalysts, including coal char or ash.

SECTION 4

CRACKING OF UNDESIRABLE AROMATIC AND SULFUR CONTAINING COMPOUNDS PRODUCED IN COAL GASIFICATION

One method of reducing the level of organic compounds in gasifier quench water, as well as heavy organic material carried downstream of the quench, is by hydrocracking these compounds in the vapor phase prior to the quench unit. However, hydrocracking will require a catalyst which can withstand severe conditions and high concentrations of components known to poison commercial catalysts.

Figure 1 shows a possible configuration which could be used to control heavy organic materials produced in a gasifier if a suitable catalytic material could be found. As shown in the figure, gas from the gasifier (stream [1]) at 425°C (Lurgi raw gas temperature) is used to pneumatically carry hot solids from the regenerator [3] to the heavy organic cracking reactor [4] via a pneumatic transport line [2]. In the reactor [4], the heavy organics are cracked in the presence of solid materials which are fluidized by the raw gas. The solids could be sand, coal ash, coal char, or catalysts which are known to promote cracking activity. In the cracking process, carbon is deposited on the solids. The solids are transferred from the cracker [4] to the regenerator [3] via line [5]. In the regenerator [3] the deposited carbon is burned in air [7] in order to generate process heat which is carried to cracker [4] by the solids as described previously. In the cracking process, light hydrocarbons will be produced and these will be combined with the light gas passing through the cracker to form the product gas [8] containing reduced levels of heavy hydrocarbons.

During fiscal year 1980, an experimental program was carried out to determine the catalytic activity of coal-derived and other materials towards cracking of selected compounds. The purpose was (1) to evaluate catalytic cracking as a technique for controlling undesirable compounds, and (2) to obtain a better understanding of the behavior of devolatilization products

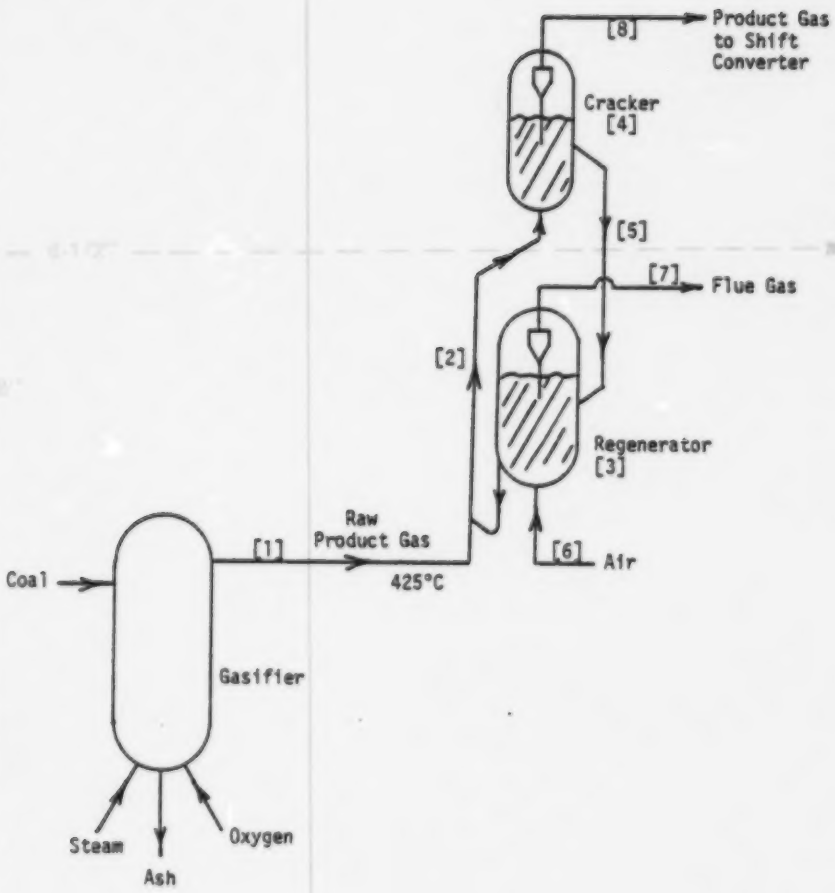


Figure 1. Potential application of gas phase cracking to controlling pollutants produced during coal gasification.

in the presence of coal-derived materials, so that variation of pollutant levels in the raw gas from various gasifiers could be rationalized.

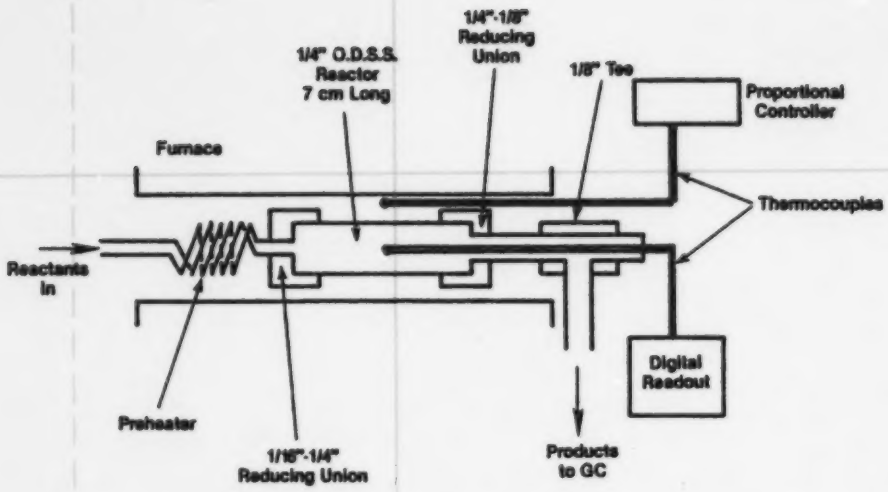
PREVIOUS WORK

Outside of the present work, the authors are aware of only one study which reported on the hydrocracking of aromatic compounds over coal char. In this study, which has been summarized by Fillo and Massey,[2] it was found that the presence of lignite char greatly enhanced the decomposition rate of phenol in comparison to the rate obtainable for the homogeneous reaction at similar conditions. Virk et al.[3] reviewed the literature on thermal hydrogenolysis (homogeneous) of aromatic compounds. Benzene decomposition was slowest and anthracene decomposition was fastest among the various aromatic compounds studied (1 to 4 rings). No alkylated aromatics were reported upon, although various other studies[4-9] have been carried out on thermal hydrodealkylation of aromatics and phenolics. In general, these studies agree with the mechanism originally proposed by Silsby and Sawyer[4] which explains the first-order dependence of the rate on the concentration of the decomposing compound and one-half order dependence on hydrogen concentration. One of their principal assumptions is equilibrium of the hydrogen dissociation reaction. According to this mechanism, the cracking of alkylated aromatics and phenols seems to involve the benzene ring as an intermediate. Based on the above observations, it appears that benzene could serve as a model compound for comparing the cracking activity of coal-derived materials. In addition to benzene, alkylated benzene compounds (toluene, ethylbenzene, and o-xylene) were chosen as model compounds for this study.

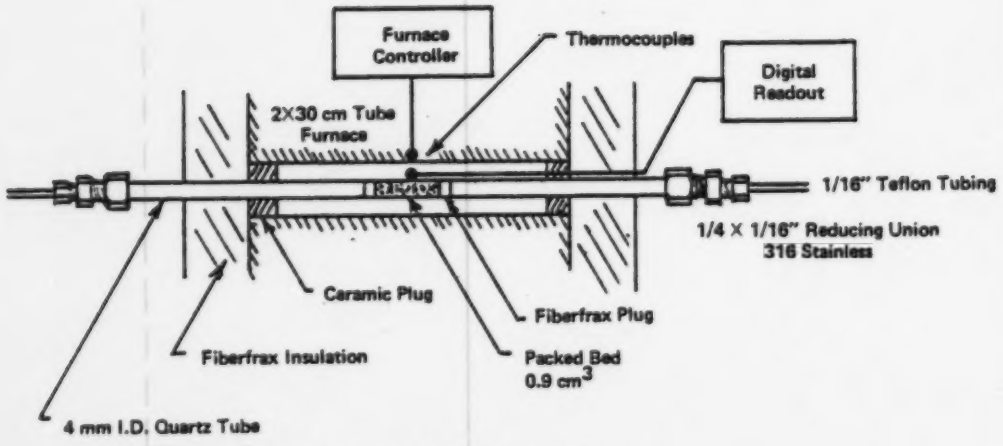
Additional discussion of previous work is given as appropriate in conjunction with the discussion of the experimental results in the following sections.

EXPERIMENTAL

RTI has carried out its experimental studies on cracking of aromatic compounds over various material in microreactors. Two different microreactors which typically held from 0.9 to 1.0 cm^3 of the material were used. These are shown in Figure 2 and are designated as either the stainless steel microreactor or the quartz microreactor.



Stainless steel microreactor



Quartz microreactor

Figure 2. Microreactor details.

The stainless steel microreactor was constructed entirely of 316 stainless steel. As shown in Figure 2, the body of this reactor was made of 1/4" (6.35 mm) tubing with 0.89 mm wall thickness. The packed length of the tube was 6 cm making the packed volume approximately 1.0 cm^3. The stainless steel microreactor was fitted with an internal 1/32" thermocouple which extended approximately halfway into the packed bed. Inlet gas to the reactor was preheated in a helix of 8 turns of 1/16" tubing, 1.27 cm I.D. The reactor assembly was positioned in the center of a 2 x 30 cm tube furnace.

The quartz microreactor was made from a 4 mm I.D. x 53 cm long quartz tube. This tube was placed in a 2 x 30 cm tube furnace with the 7 cm packed section of the quartz tube being positioned in the center of the furnace. The volume of the packed section was approximately 0.9 cm^3. All tubing leading to or from the quartz tube was 0.8 mm I.D. Teflon tubing; and fittings, such as reducing unions, were 316 stainless steel. A thermocouple was strapped to the quartz tube to measure bed temperature. Experiments showed that there were no detectable temperature gradients across the reactor.

The microreactors were supported by the microreactor system shown in Figure 3. Feed gas for the reactors was prepared by blending high purity hydrogen with mixtures of various hydrocarbons in nitrogen. These mixtures were:

1. 290 ppm benzene, 52.2 ppm toluene, 9.87 ppm ethylbenzene, and 11.4 ppm o-xylene in nitrogen.
2. 269 ppm benzene in nitrogen.
3. 88.2 ppm thiophene in nitrogen.

The gases were blended to maintain the hydrogen-nitrogen ratio of approximately 1.0. In most experiments (except where noted in this report) the total gas flow to the microreactors was 30 cm^3 (standard) per minute. The pressure at the inlet of the microreactors was essentially atmospheric pressure and may have reached 2 psig under some conditions of testing.

As shown in Figure 3, provisior was made for bypassing the reactor so that the inlet and outlet concentration of the hydrocarbons in the feed gas could be determined. Analyses of reactants and products were carried out by gas-liquid chromatography. A Perkin-Elmer 3920B gas chromatograph with FID was used with a 244 cm x 3.2 mm stainless steel column packed with tris-1,2,3-cyanoethoxypropane on 80/100 mesh Chromosorb P. A helium carrier gas

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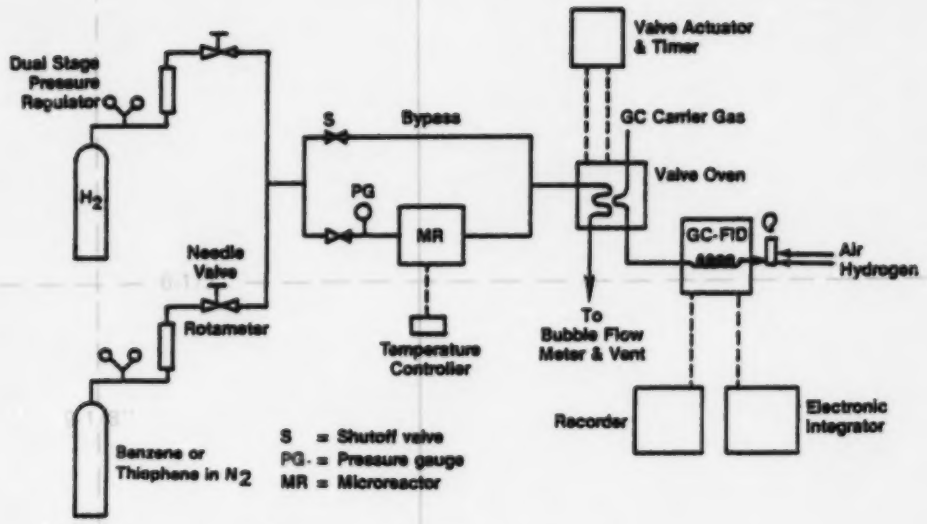

Figure 3. Microreactor and supporting system.

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with a flow of 20 cm^3/min was used and the column was held at 85°C. Gas samples of 1.0 ml were injected into the chromatograph at 10 minute intervals using a zero volume six-port stainless steel Carle valve.

The proximate and ultimate analysis of the coal-derived material used in the cracking studies is shown in Table 1. Each material was crushed and screened to 28 x 48 mesh and then loaded into the microreactors.

RESULTS AND DISCUSSION

The results of the cracking studies can be grouped into three distinct groups of experiments.

1. Studies on hydrocracking of the benzene-alkylbenzene mixture over coal-derived materials in the stainless steel microreactors.
2. Studies on hydrocracking of benzene and thiophene over coal-derived materials in the quartz microreactor.
3. Studies on hydrocracking of benzene and thiophene over metal-containing materials in the quartz microreactor.

Cracking of a Benzene-Alkylbenzene Mixture Over Coal-Derived Materials in the Stainless Steel Microreactor

In this experimental study with benzene and three alkylated benzenes present in the feed gas, a full description of the kinetics would be extremely complex since so many possible parallel and series reactions can occur. To limit the complexity of the data analysis, a simple first-order decomposition of each component is assumed. This is probably reasonable for ethylbenzene and o-xylene; however, the assumption could lead to underestimation of the benzene and toluene cracking rates. Justification for the simplified analysis is that (1) the amount of ethylbenzene and o-xylene in comparison to benzene is small and should not contribute significantly to the apparent rate of benzene decomposition, (2) at high decomposition rates of benzene, ignoring benzene production from the other aromatics will result in small errors in the apparent rate of decomposition since the benzene concentration is almost six times that of any other component, and (3) an upper bound of the benzene decomposition rate can be estimated as discussed toward the end of this section.

In previous studies[2-7] of hydrocracking, hydrogenolysis, or hydrodealkylation of aromatic compounds, the data obtained are correlated using a

TABLE 1. ANALYSES OF COAL-DERIVED MATERIALS USED IN MICROREACTOR TESTS

	Peabody Char	Illinois No.6 Char	Wyoming Char	Pyrolyzed Wyoming Coal	Wyoming Ash
Proximate (wt. % as received)					
Moisture	1.46	0.77	1.27	0.75	1.07
Volatile Matter	1.73	2.56	5.39	7.66	3.15
Fixed Carbon	84.61	39.94	36.03	80.76	9.53
Ash	12.30	56.73	56.81	10.83	86.25
Ultimate (wt. % as received)					
Carbon	82.34	39.61	40.53	81.54	9.60
Hydrogen	0.84	0.59	0.46	1.89	0.51
Nitrogen	1.17	0.72	0.44	1.17	0.34
Sulfur	2.06	1.56	0.48	0.52	0.28
Oxygen (by difference)	1.41	0.79	1.28	4.05	3.02
Source of Material	Coke produced by Peabody Coal Company from Kentucky No.11 at 870 to 1090°C.	Residue from batch gasification at 950°C. RTI gasifier.	Residue from continuous gasification at 950°C. RTI gasifier.	Coal pyrolyzed at 835°C maximum and 13.6 atm. RTI gasifier.	Coal gasified at 950°C with steam and air. High carbon conversion. RTI gasifier.

rate expression which was first order with respect to the compound being decomposed and one-half order with respect to the hydrogen concentration. Since in all experiments of this study a constant hydrogen mole fraction was maintained, the rate can be expressed in terms of a pseudo first-order rate constant containing the hydrogen term. Assuming a plug flow reactor with negligible change in gas volume with extent of decomposition, the integrated material balance under isothermal conditions for the j^{th} component can be written as

$$k_j = \frac{1}{\tau} \ln \frac{C_{ji}}{C_{jo}} \qquad (1)$$

where

τ = space-time, sec

C_{ji}, C_{jo} = inlet and outlet concentrations of the j^{th} component, g mole/cm^3

k_j = first-order rate constant for the j^{th} component, sec^{-1}.

This equation was used to calculate the first-order rate constants for all experiments in order that the relative activity of the packing material toward cracking of aromatics could be compared with the empty reactor activity and published homogeneous decomposition rates. For each packing material, rate constants were determined at a series of temperatures. Arrhenius plots of the first-order rate constants for the individual compounds are shown in Figures 4-7 and are compared with existing literature data. Table 2 gives the least squares estimates of the preexponential factors and activation energies.

Examination of Figures 4-7 shows that the steady-state cracking activity obtained in the empty bed experiments is unusually high being 1 to 2 orders of magnitude greater than homogeneous first-order constants reported in the literature. The empty bed experiments reported in this paper were carried out in reactors that had high surface-to-volume ratios (about 3-6 times those used in previous studies).[2-9] Also, the activity appeared to increase rapidly with run time as seen in Figure 8. Apparently, the surface of the stainless steel reactor is increasing in activity under the reducing action of hydrogen and possible carbon laydown (in some unknown form), and the activity reaches a steady-state value after extended time periods (on the order of 12-24 hours).

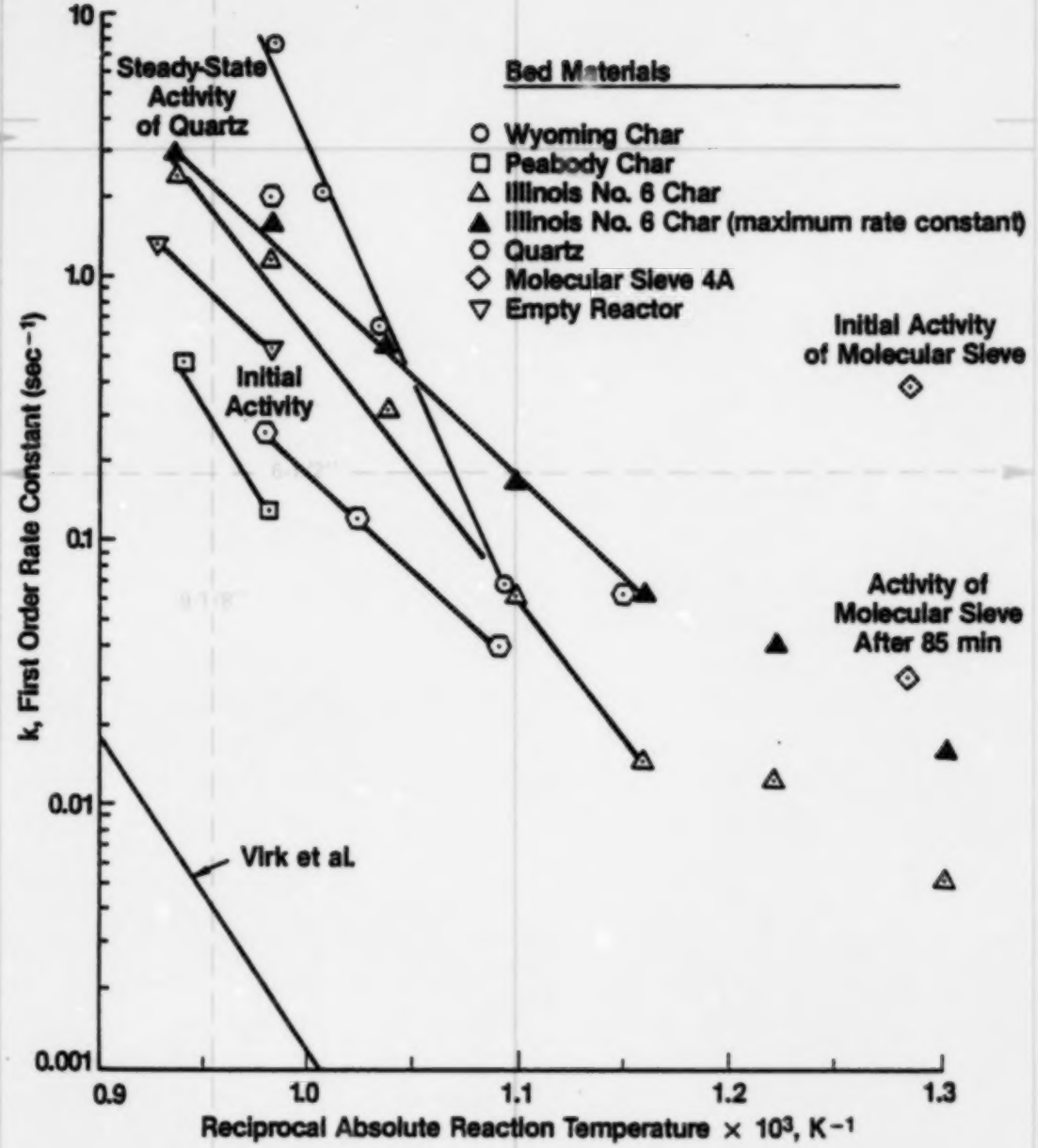

Figure 4. Rate constants for benzene hydrocracking.

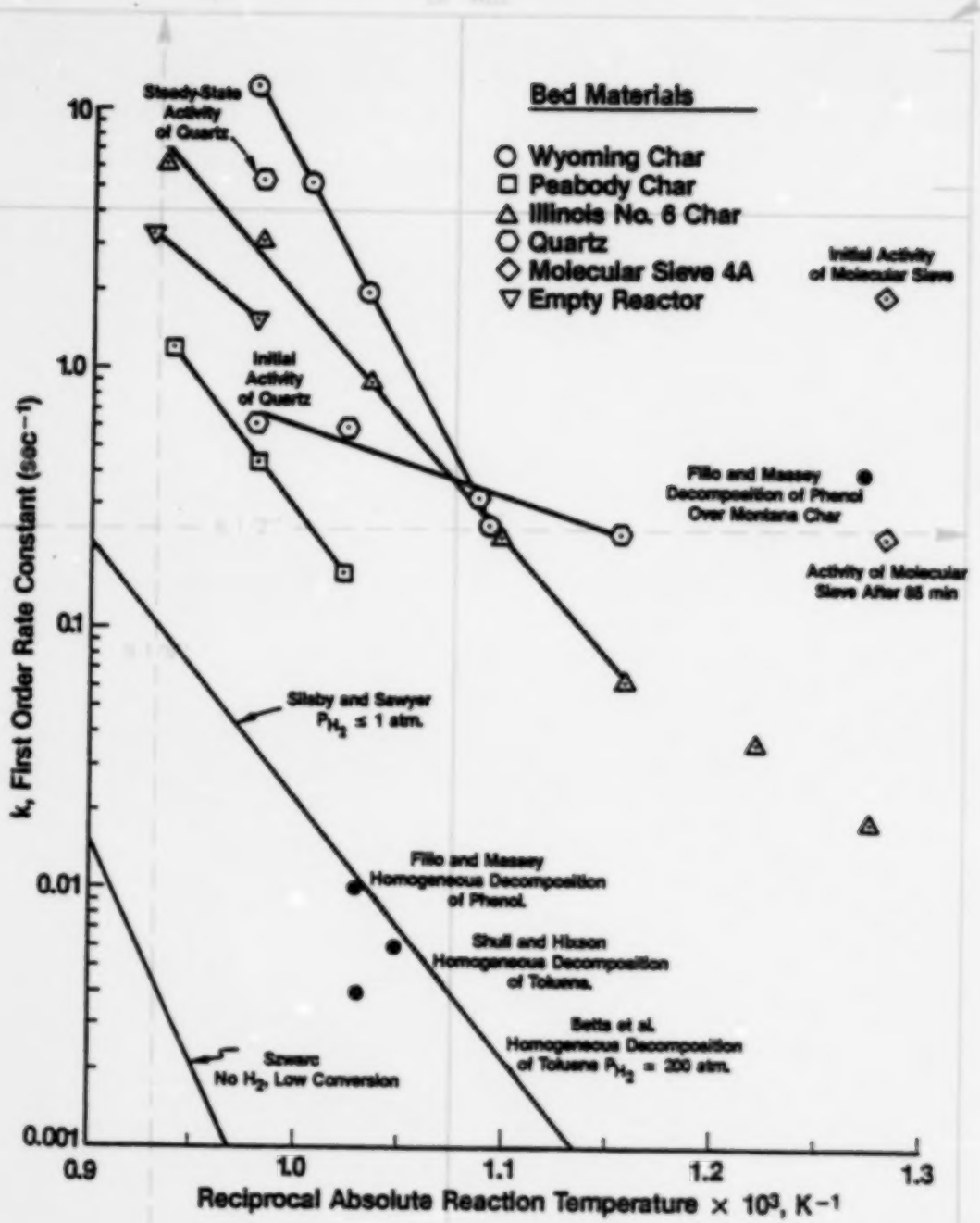

Figure 5. Rate constants for toluene hydrocracking.

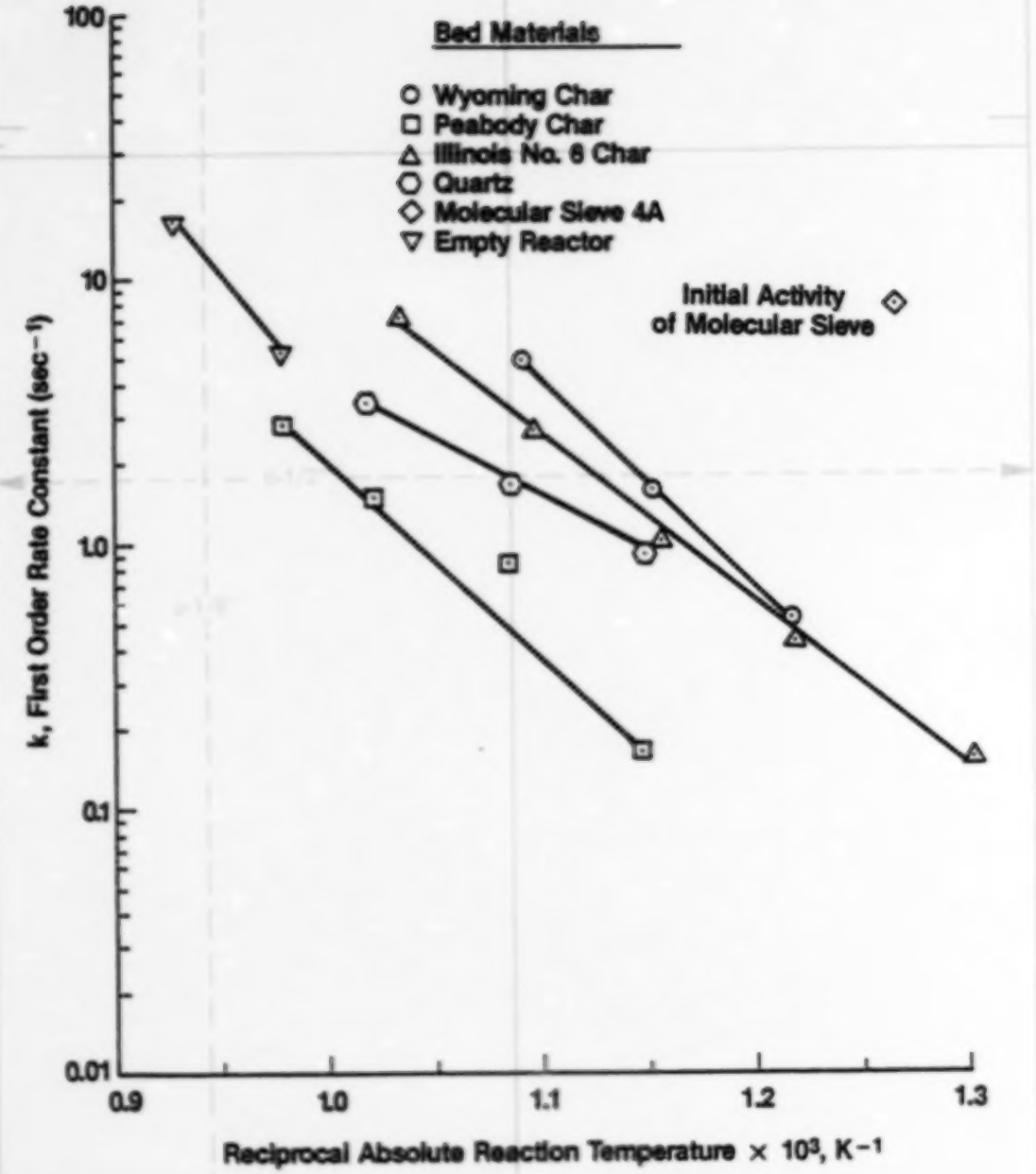

Figure 6. Rate constants for ethylbenzene hydrocracking.

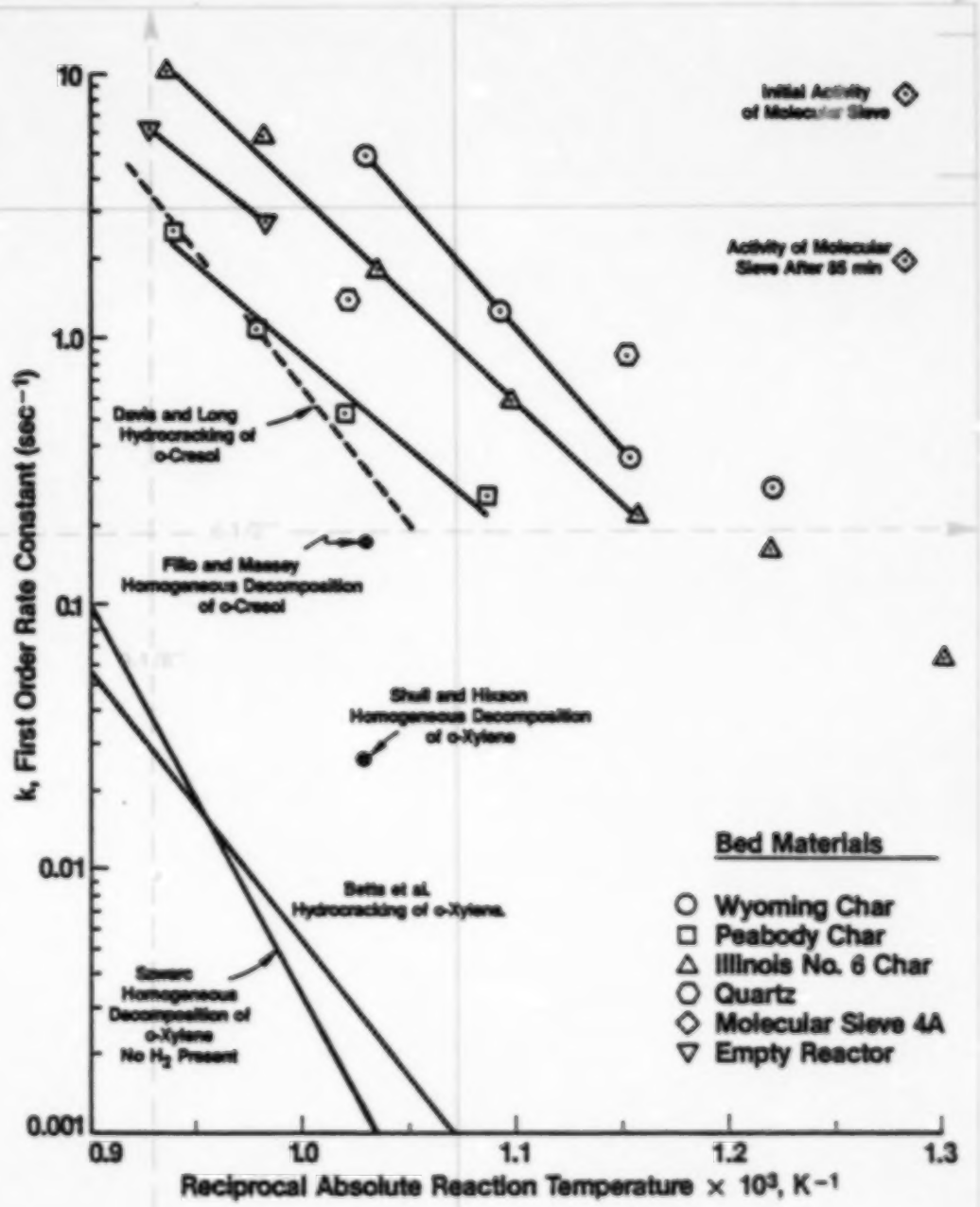

Figure 7. Rate constants for o-xylene hydrocracking.

TABLE 2. ARRHENIUS EQUATIONS FOR HYDROCRACKING

Compound	Material	Arrhenius Equations $k = k_o e^{-E/RT} (sec)^{-1}$
benzene	Wyoming char	1.71×10^{18} exp (-81290/RT)
	Illinois No.6 char+	1.05×10^{10} exp (-46730/RT)
	Peabody char	3.29×10^{11} exp (-57840/RT)
	quartz*	4.61×10^{6} exp (-33920/RT)
	empty reactor**	3.38×10^{7} exp (-36510/RT)
toluene	Wyoming char	5.29×10^{15} exp (-68410/RT)
	Illinois No.6 char	2.32×10^{9} exp (-41740/RT)
	Peabody char	5.35×10^{2} exp (-47000/RT)
	quartz*	2.98×10^{6} exp (-12360/RT)
	empty reactor**	7.21×10^{6} exp (-31250/RT)
o-xylene	Wyoming char	1.97×10^{10} exp (-42960/RT)
	Illinois No.6 char	2.17×10^{8} exp (-35710/RT)
	Peabody char	8.01×10^{6} exp (-31890/RT)
	quartz*	scatter
	empty reactor**	1.75×10^{7} exp (-31830/RT)
ethylbenzene	Wyoming char	1.51×10^{9} exp (-34640/RT)
	Illinois No.6 char	2.39×10^{7} exp (-29000/RT)
	Peabody char	5.59×10^{7} exp (-34030/RT)
	quartz*	8.05×10^{4} exp (-19610/RT)
	empty reactor**	2.06×10^{10} exp (-44830/RT)

* Initial rate.
** Steady-state rate.
+ Expression for maximum $k = 3.38 \times 10^{7}$ exp (-36510/RT).
E = Activation energy, cal/g mole.
R = Gas constant, cal/(g mole °K).

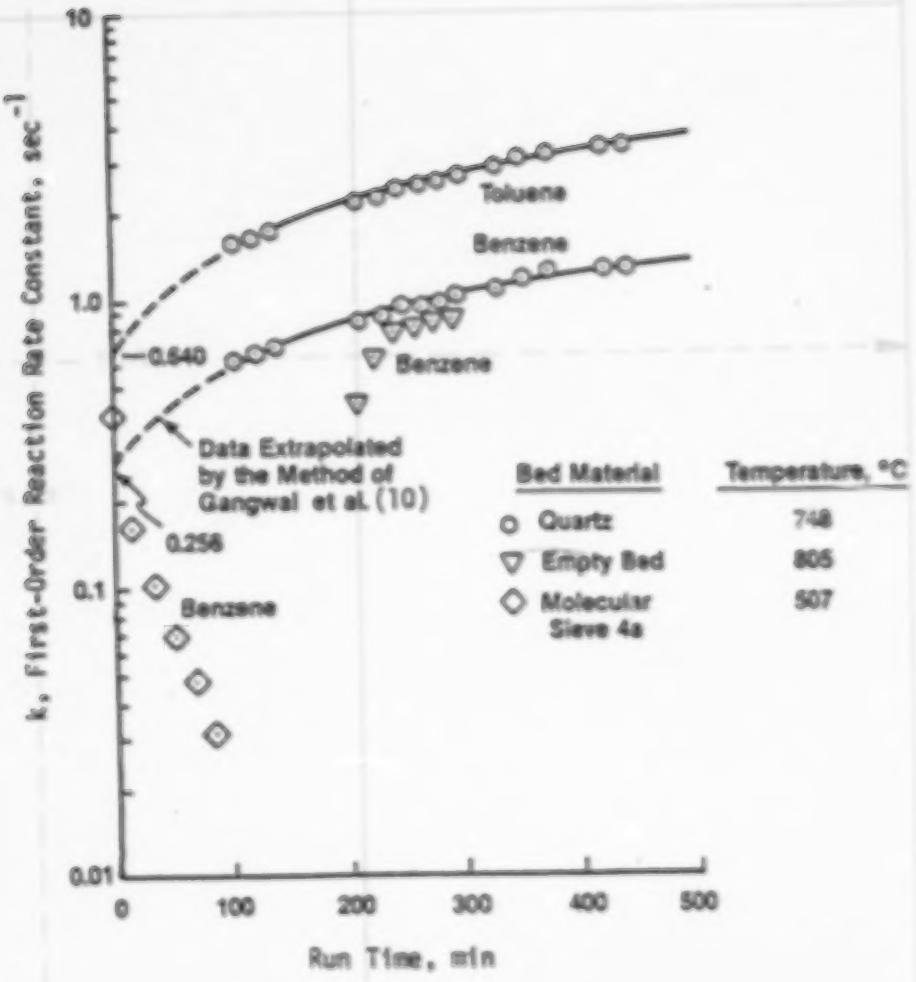

Figure 8. Time-dependent behavior of the first-order rate constant.

Comparing the steady-state empty bed constants to the first-order rate constants associated with each char (which shows no time-dependent activity after overnight conditioning), it can be seen that the Wyoming and Illinois No.6 chars show enhanced cracking activity over the empty reactor. The Peabody char showed significantly lower activity, and quartz had a lower initial activity than the empty bed, demonstrating that the packing material blinded in part the activity of the stainless steel reactor wall. Consequently, the rate constants associated with the Wyoming and Illinois No.6 chars are significantly higher than the homogeneous rate constants and more than two orders of magnitude higher than the homogeneous rates reported previously in the literature.

Quartz was used in the microreactor for the purpose of comparison because it was initially thought that it would be relatively inert and would have a packed bed voidage similar to the chars. However, the initial activity of quartz showed rate constants at least an order of magnitude higher than homogeneous rate constants reported in the literature. Furthermore, the rate constants were observed to increase with run time at 748°C, and over a 24-hour period the rate constants for benzene and toluene increased by an order of magnitude. The time-dependent behavior of these constants are shown in Figure 8. The steady-state rate constants for benzene and toluene over quartz were 1.95 and 5.59 sec^{-1}, respectively. The initial rate constants for the decomposition of benzene and toluene over quartz were obtained by extrapolating the data by the method of Gangwal et al.[10] Material balances for carbon showed that carbon (in some form) was being deposited on the quartz over the 24-hour period. It is possible that the deposited material was catalyzing the cracking of the benzene and toluene. After the 24-hour period at 748°C the temperature of the reactor was lowered to 650°C, but no enhancement in activity over previous experiments at 650°C was observed; i.e., whatever was being formed at 748°C was not active at 650°C.

Molecular sieve 4A was also used as a packing material and showed very high initial cracking activity in comparison to the other packing materials investigated, as can be seen in Figures 4-7. However, this activity quickly faded (Figure 8) with coke deposits blocking the porous structure of the sieve being a probable deactivation mechanism.

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Based on the data presented in Figure 4-7, the following additional observations can be made:

1. For a given volume of packing material and the same operating conditions, the rate of cracking of the aromatic compounds is in the order: ethylbenzene > o-xylene > toluene > benzene.
2. For a given aromatic compound and the same operating conditions with temperatures greater than 600°C, the activity of the char toward enhancing decomposition of compounds is in the order: Wyoming char > Illinois No.6 char > Peabody char.

The theoretical activation energy for homogeneous hydrodealkylation of alkylated aromatics is 50 ± 5 kcal/mole, based on the hydrogen dissociation mechanism originally proposed by Silsby and Sawyer.[4] The experimental values reported are generally 45-50 kcal/mole for toluene hydrodealkylation.[4-7] However, the empty bed activation energy for toluene (Table 2) is significantly lower, i.e., 31 kcal/mole, substantiating in part that the catalytic nature of the stainless steel reactor may be responsible. Virk et al.[3] reported an activation energy of 52.6 kcal/mole for homogeneous hydrogenolysis of benzene. Again, the empty bed activation energy for benzene is much lower. The heterogeneous hydrocracking reactions of benzene and toluene over the Wyoming char show significantly higher activation energies of 81 and 68 kcal/mole, respectively. The values are close to those reported by Szwarc[8] whose experiments were carried out in the absence of hydrogen. Thus the heterogeneous reaction may be proceeding by a mechanism which is entirely different from the homogeneous reaction. The Illinois and Peabody chars have activation energies associated with the decomposition of benzene and toluene which are considerably lower than those observed for the Wyoming char. One explanation for this is that the Wyoming char reaction rate is not limited by internal diffusion, whereas the reaction rate for other chars might be. For an internal diffusion limited first-order reaction, the apparent activation energy is one-half of the true activation energy; this could explain in part the lower values observed for the Illinois and Peabody chars. This reasoning is supported by the experiments of Walker and coworkers[11-13] who have shown that low rank chars generally have an ample supply of feeder and transitional pores, whereas bituminous and higher rank chars do not.

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In order to support the hypothesis that cracking rates over the Illinois and Peabody chars were limited by internal diffusion whereas the rates over Wyoming char was not, physical properties of the chars measured using a BET surface area analyzer and a mercury porosimeter. Nitrogen was used as the adsorbate for the BET surface area and pore volume measurements. The mercury porosimeter had a total pressure penetrative range from 0 to 60,000 psi for pore size distribution measurements. In addition, true density measurements were made using a helium pycnometer. The results from these measurements are shown in Table 3 and Figures 9 and 10.

From Table 3, it can be seen that the three chars have N_2-BET surface areas and pore volumes. It is well known from the literature[11-13] that nitrogen does not penetrate the very fine pores. Thus, the N_2-BET method may result in an underestimation of the true surface areas of coal chars which possess microporosity. Although all coal chars are known to possess microporosity, according to Walker and coworkers,[11-13] the low rank chars (e.g., the Wyoming char) contain an ample supply of macro and feeder pores as opposed to the high rank chars (e.g., the Illinois No.6 and Peabody chars). This makes it easier for gas molecules to penetrate to a greater distance into the micropores of low rank chars. Consequently the N_2-BET method resulted in a large range of surface areas for the chars studied. On the other hand, the mercury porosimetry method resulted in a comparatively much smaller spread as seen from Table 3. Cumulative surface area and pore volume of the three chars are plotted as a function of inverse pore diameters in Figures 9 and 10, respectively. In Figure 9, it can be seen that the Wyoming char has the greatest number of transitional pores, followed by the Illinois No.6 char and finally by the Peabody char. The order of cracking activity is also the same. Further, in Figure 10 most of the pore volume lies in the big pores for the Illinois No.6 and the Peabody char, whereas the pore volume for the Wyoming char can be substantially attributed to transitional pores leading up to the fine pores. All these measurements lend support to the hypothesis that cracking rates on the Illinois No.6 and Peabody chars may be limited by internal diffusion; whereas this may not be the case for the Wyoming char.

An upper bound on the benzene decomposition rate on Illinois No.6 char is shown in Figure 4 by the dark triangles. This is calculated assuming

TABLE 3. PHYSICAL PROPERTIES OF COAL CHARS

Coal Char	Surface Area m^2/g		Pore Volume cm^3/g		True (Helium) Density g/cm^3
	N_2-BET	Mercury Porosimetry	N_2-BET	Mercury Porosimetry	
Wyoming	299	55	0.21	0.74	2.45
Illinois No.6	76	28	0.04	0.60	2.56
Peabody	3.4	20	0.005	0.37	1.92

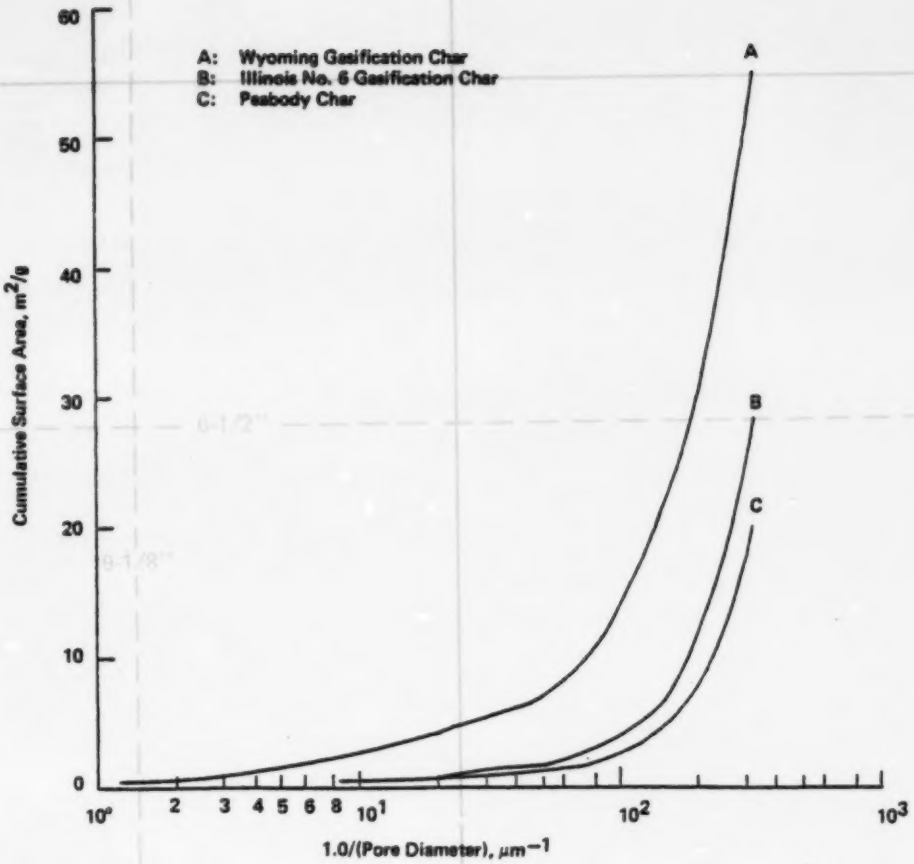

Figure 9. Cumulative surface area of chars by mercury porosimetry vs. inverse pore diameter.

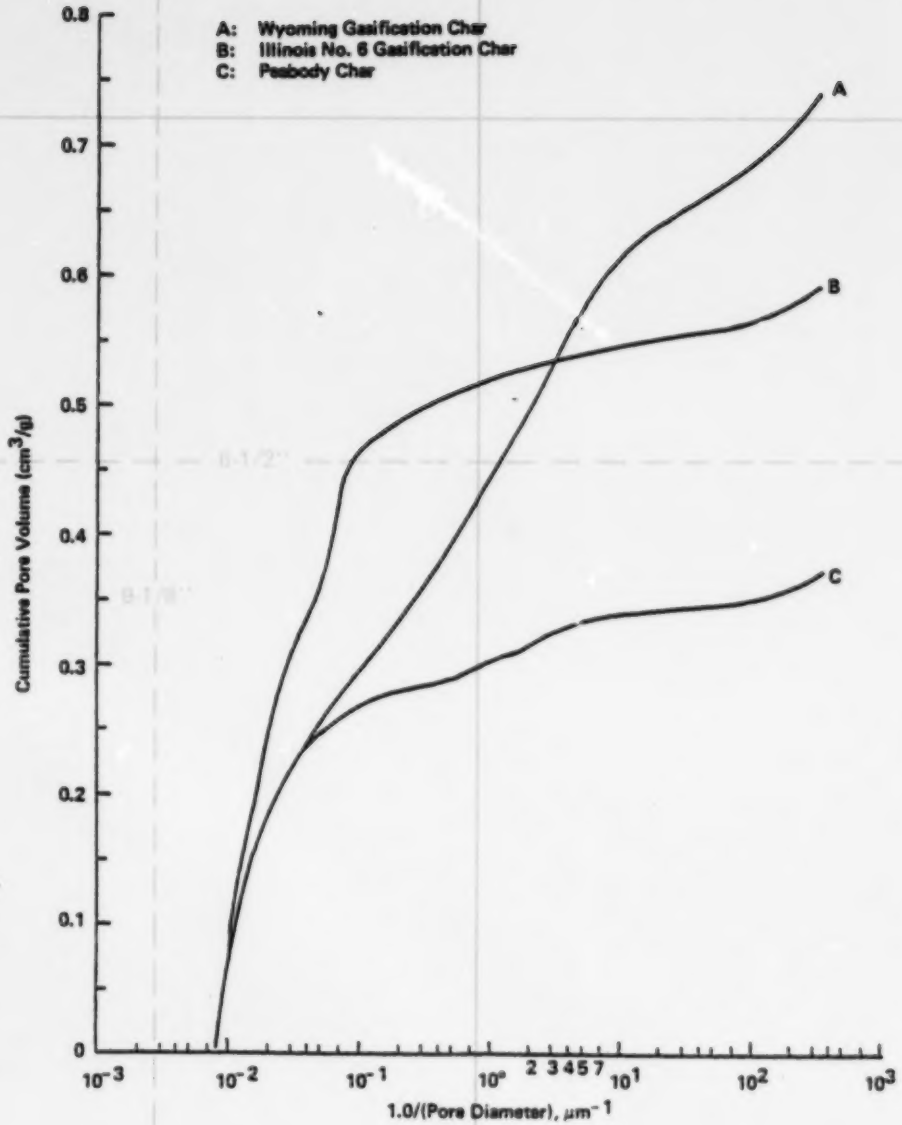

Figure 10. Cumulative pore volume of chars by mercury porosimetry vs. inverse pore diameter.

that benzene is an intermediate product from the cracking of the other aromatics present in the feed. When compared to the apparent rate (i.e., empty triangles), it can be seen that even higher rates of benzene decomposition exist if the assumption is true. The activation energy, however, is lower--i.e., 36.5 compared to 46.7 (see Table 2, footnote)--and thus as the temperature increases, the observed rate and the maximum possible rate approach each other.

The major gaseous product of decomposition of the aromatic compounds appeared to be light gases (probably mostly methane) although the GC column used in the experiments could not separate CH_4, C_2H_6, and C_2H_4. Much more methane was formed than could be accounted for by the removal of methyl groups from the alkylated benzene compounds. Also, carbon balances showed that substantial quantities of the input carbon remained in the reactor. The only exception to this was in the case of the Wyoming char experiments run at 748° and 800°C. In these cases carbon in the char also was converted to light gases (probably methane). The activation energy of this conversion was on the order of 104 kcal/g mole which corresponds to the temperature dependency of the equilibrium constant for hydrogen dissociation.

Cracking of Benzene and Thiophene Over Coal-Derived Materials in the Quartz Microreactor

The results of this study are shown in Figure 11. In this figure, a comparison is made between the first-order rate constant for the homogeneous hydrocracking of benzene reported by Virk et al.[3] and that determined in RTI's quartz microreactor using an empty quartz tube. It can be seen that the rate constant determined in the microreactor is approximately a factor of 7 greater than Virk's value. One reason for this discrepancy is that the space-time used to compute the rate constant was based on 7 cm of the quartz tube rather than its total heated length. Assuming that the quartz tube was isothermal over its heated length would reduce the ratio of the computed rate constant to that reported by Virk to 1.6. However, because the cracking rate reported by Virk et al.[3] and that determined in the empty quartz tube are many orders of magnitude lower in comparison to the cracking rates over coal-derived materials, little error is introduced in the calculation of the rate constant associated with the packing materials when cracking in the

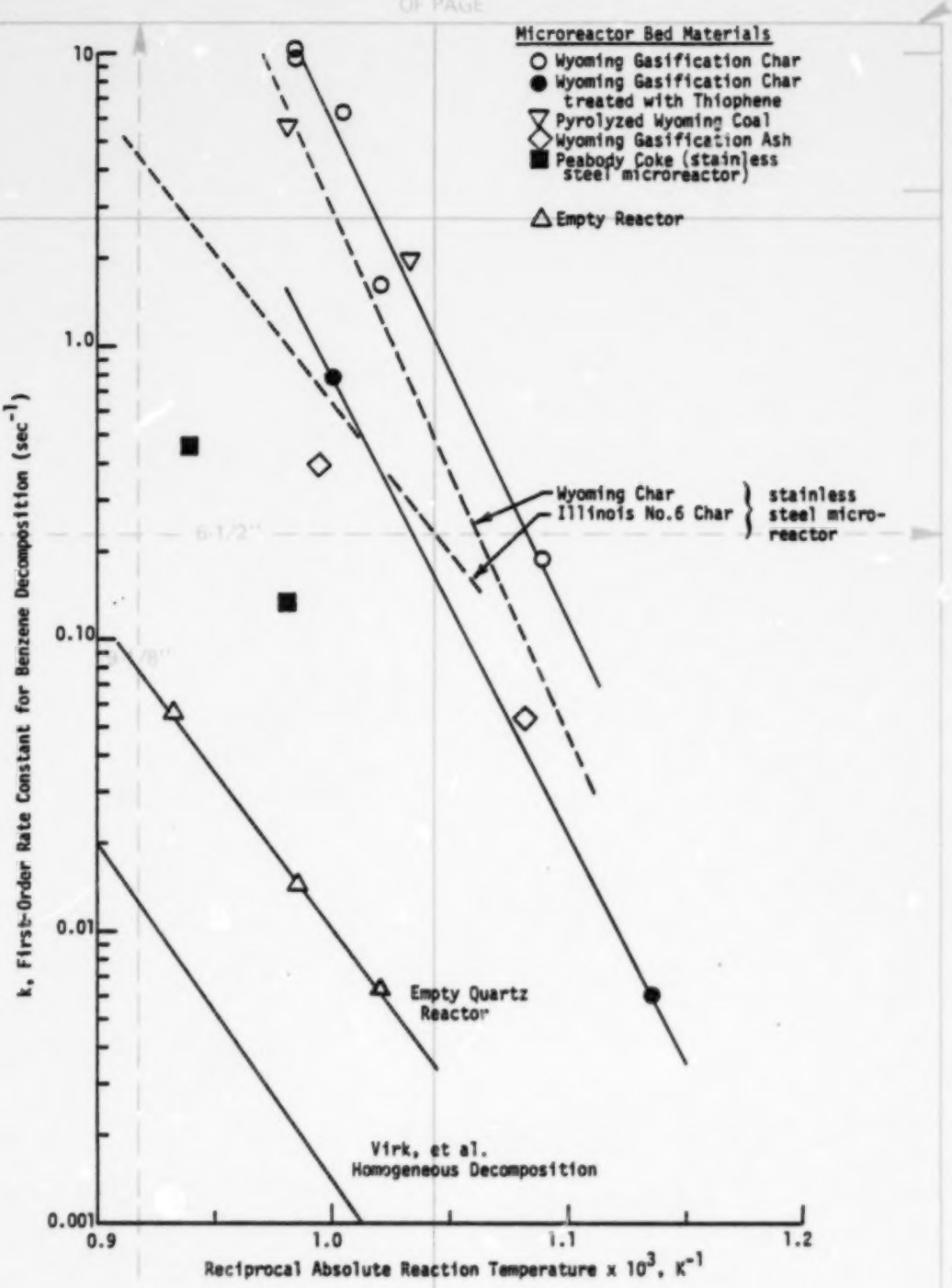

Figure 11. Rate constants for benzene hydrocracking over coal-derived materials.

empty section of the quartz tube outside the packed bed is ignored. Another reason for the discrepancy could perhaps be due to the extremely low conversion in the empty quartz reactor leading to analytical difficulties in determining a real difference between the inlet and outlet concentration of benzene.

In the previous section, the decomposition of benzene in a mixture of benzene, toluene, ethylbenzene, o-xylene, hydrogen, and nitrogen over various coal-derived materials in a stainless steel microreactor was reported. It was recognized that the stainless steel wall itself showed strong catalytic activity toward cracking of aromatic compounds but that this activity was blinded in part when packing materials were used in the reactor. The first-order rate constants determined in the quartz microreactor for several coal-derived materials are compared in Figure 11 to the previous results in stainless steel microreactors. The agreement for Wyoming chars are within a factor of two. The Wyoming ash (which contains little carbon and consequently low surface area) has an activity which is a factor of four to eight times lower than the pyrolyzed Wyoming coal and Wyoming char which contained at least 40 percent carbon.

Experiments were carried out to determine the rate of cracking of sulfur compounds over Wyoming char. Thiophene was used as a model compound in the quartz microreactor packed with Wyoming gasification residue. The microreactor was operated at 607°C and was fed with a gas mixture containing approximately 50 percent hydrogen and nitrogen each and 44 ppm of thiophene. The total gas feed rate was 30 cm^3/min and the reactor pressure was approximately atmospheric. The Wyoming char showed considerable initial activity toward cracking the thiophene with a first-order rate constant of 12.4 sec^{-1}. This is about three orders of magnitude greater than the rate constant for the cracking of benzene over the same char. After the high initial activity, the catalytic activity of the char decreased rapidly; and after 19 hours of operation, the first-order rate constant had fallen to 1.99 sec^{-1} (a factor of 6.2 from its initial activity). At the end of 19 hours, the feed gas was switched back to the benzene-nitrogen-hydrogen mixture. Examination of Figure 11 shows that the benzene cracking activity of the Wyoming char was also reduced by a factor of 6 to 8 depending on the temperature; this suggests that the thiophene had possibly poisoned many of the active cracking sites on the char surface.

Since raw coal gas contains many sulfur compounds as well as thiophene, the mechanism of the destruction of organic compounds within a coal gasifier will be complex. Based on the benzene data given in Figure 11, rough estimates of the destruction of aromatic compounds can be obtained. For example, let it be assumed that devolatilization of the coal takes place at 700°C in a fluidized bed gasifier at 600 psia with 15 percent hydrogen in the gas and that the gas residence time in the bed is 1.0 sec. Using the curve in Figure 11 corresponding to the Wyoming char that was poisoned by thiophene, a benzene decomposition of 58 percent is estimated. At 725°C, 91 percent of the benzene would be decomposed. Since many of the other aromatic compounds have cracking rates much higher than benzene, an even higher percentage decomposition of these compounds would be expected. On the other hand, in the Lurgi gasifier or in the free-fall SYNTHANE gasifier where a majority of the coal devolatilization takes place at temperatures less than 500°C, practically no decomposition of aromatics would be expected.

These observations are substantiated by actual gasifier experience on the SYNTHANE process. Lewis et al.[14] reported that by feeding Montana Rosebud coal directly to a fluidized bed gasifier operating at 780°C, the phenol content of the condensate was reduced from several thousand ppm for free-fall feeding to only a few ppm. Also for the direct feeding of coal to the bed, no evidence of tars was found in the gasifier system, whereas over 3 percent of the coal was converted to tars in the free-fall mode of feeding where devolatilization takes place at low temperatures.

Based on the benzene cracking data obtained in the microreactor, it does not appear that the char bed concept for cracking aromatic compounds (and thus producing a cleaner wastewater) could be effective at temperatures much below 700°C. Since a gasifier with an outlet temperature of 750°C or greater would probably be free of pollutants based on the above calculations, a char bed cracker would not be necessary in this situation. Based on this argument, RTI has screened several cracking and hydrodesulfurization catalysts, which are capable of operating at lower temperatures (e.g., 400° to 500°C), for use in a vapor phase cracking process for pollutant control in coal gasification processes. These studies are reported in the next section.

Cracking of Benzene and Thiophene Over Iron- and Nickel-Containing Materials in the Quartz Microreactor

As noted in previous sections, the wall of the stainless steel microreactor showed substantial activity toward the hydrocracking of aromatic compounds, and the temperature required for cracking over coal-derived material was out of the practical range unless the outlet temperature of the gasifier was over 700°C. In this case treatment of the gas would most likely not be necessary. For these reasons, attention was focused on materials containing nickel and iron and several catalysts containing these elements.

Hydrocracking of benzene has been studied over (1) steel wool, (2) iron turnings, (3) nickel filings, (4) 316 stainless steel, (5) triply-promoted iron oxide NH_3 synthesis catalyst, and (5) nickel molybdate hydrodesulfurization/hydrodenitrogenation (HDS/HDN) catalyst. The compositions of the NH_3 synthesis catalyst and the HDS/HDN catalyst are shown in Tables 4 and 5, respectively.

These studies were performed in the quartz microreactor at approximately atmospheric pressure and 300° to 500°C. Approximately 0.9 cm^3 of material, 28 x 48 mesh, was packed into the reactor. The exception to this was in the case of steel wool. In this case 0.21g of No.0000 commercial grade carbon steel wool was packed into the 0.9 cm^3 reactor volume. For comparison, 0.9 cm^3 of the NH_3 synthesis catalyst weighed 2.17g. In most of the experiments, the feed gas composition was approximately 50 percent H_2 and N_2 with 135 ppm benzene. The feed gas flow rate was 30 cm^3 (standard)/min for a space velocity of 2000 hr^{-1}. For the triply-promoted iron oxide catalyst, two space velocities of 2000 and 4000 hr^{-1} were used. In order to increase catalytic activity, it was necessary to oxidize the first four materials listed above. Oxidation was carried out by passing air through the reactor at a space velocity of 1000 hr^{-1} and 450°C for 15 min. It was not necessary to activate the promoted iron oxide catalyst with air. Following the oxidation step, the fully activated form of the catalyst was obtained by passing the benzene-N_2-H_2 mixture over the catalyst at 450°C and a space velocity of 2000 hr^{-1}. The ammonia synthesis catalyst obtained approximately 67 percent of full activity in 170 min and reached full activity in 28 hr. A more rapid activation could possibly be achieved at higher temperature, space velocity, and concentration of organic species in the feed gas. It was

TABLE 4. COMPOSITION OF NH_3 SYNTHESIS CATALYST

	Wt%
FeO	30-37
Fe_2O_3	65-58
Al_2O_3	2.0-3.0
K_2O	0.5-0.8
CaO	0.7-1.2
SiO_2	<0.4

TABLE 5. COMPOSITION OF HDS/HDN CATALYST

	Wt%
MoO_3	15
NiO_2	3.0
SiO_2	4.5
Na_2O	0.1
Al_2O_3	balance

found that hydrogen alone was not sufficient for activation. Carbon in some form, in this case available from benzene, was necessary for the activation. The activity of the fully active catalyst decreased in pure hydrogen in the absence of benzene but increased to former levels when benzene flow to the reactor was reestablished. The HDS/HDN catalyst was activated by passing a mixture of 50 percent hydrogen and nitrogen with 44 ppm thiophene over the catalyst at 300°C and a space velocity of 2000 hr^{-1} for 24 hr.

The results of the benzene cracking studies are shown in Figure 12. Using Equation (1), pseudo first-order reaction rate constants were obtained for benzene hydrocracking. Arrhenius plots relating the rate constants to reaction temperature were developed for the stainless steel, steel wool, and NH_3 synthesis catalysts and are shown in the figure. It can be seen that the activated steel wool and NH_3 synthesis catalysts are the most promising cracking catalysts, as indicated by the first-order rate constants. The steel wool and NH_3 synthesis catalyst at space velocity of 2000 hr^{-1} (30 cm^3/min flow rate to the microreactor) have similar rate constants as a function of temperature. The reason for this is not clear since significantly different masses of the catalysts were used. One explanation could be that, by coincidence, the two differing amounts of catalysts could have had similar surface characteristics.

A second series of experiments were carried out with the NH_3 synthesis catalyst. In this series, a space velocity of 4000 hr^{-1} was used in an effort to reduce mass transfer effects which are indicated by the curvature of the data in Figure 12, at a space velocity of 2000 hr^{-1}. Instead of obtaining increased rate constants at the higher space velocity, the rate constants were decreased by a factor of two in some cases. Examination of this phenomena revealed that the level of activity of the NH_3 catalyst was a function of its history and the length of time that a catalyst was held at a specified temperature with the benzene-nitrogen-hydrogen mixture passing through it. An example of this is the experiment with the ammonia catalyst at 383°C and a space velocity of 2000 hr^{-1}. In this case a detailed history of the catalyst's activity was recorded. Prior to this experiment the catalyst was tested at 462°C. The initial activity at 383°C ($1/T = 15.24 \times 10^{-4}(°K)^{-1}$) was high with $k = 6.66$ sec^{-1}, as shown in Figure 12. However, the rate constant fell to $k = 4.41$ sec^{-1} after 2 hr on stream at 383°C.

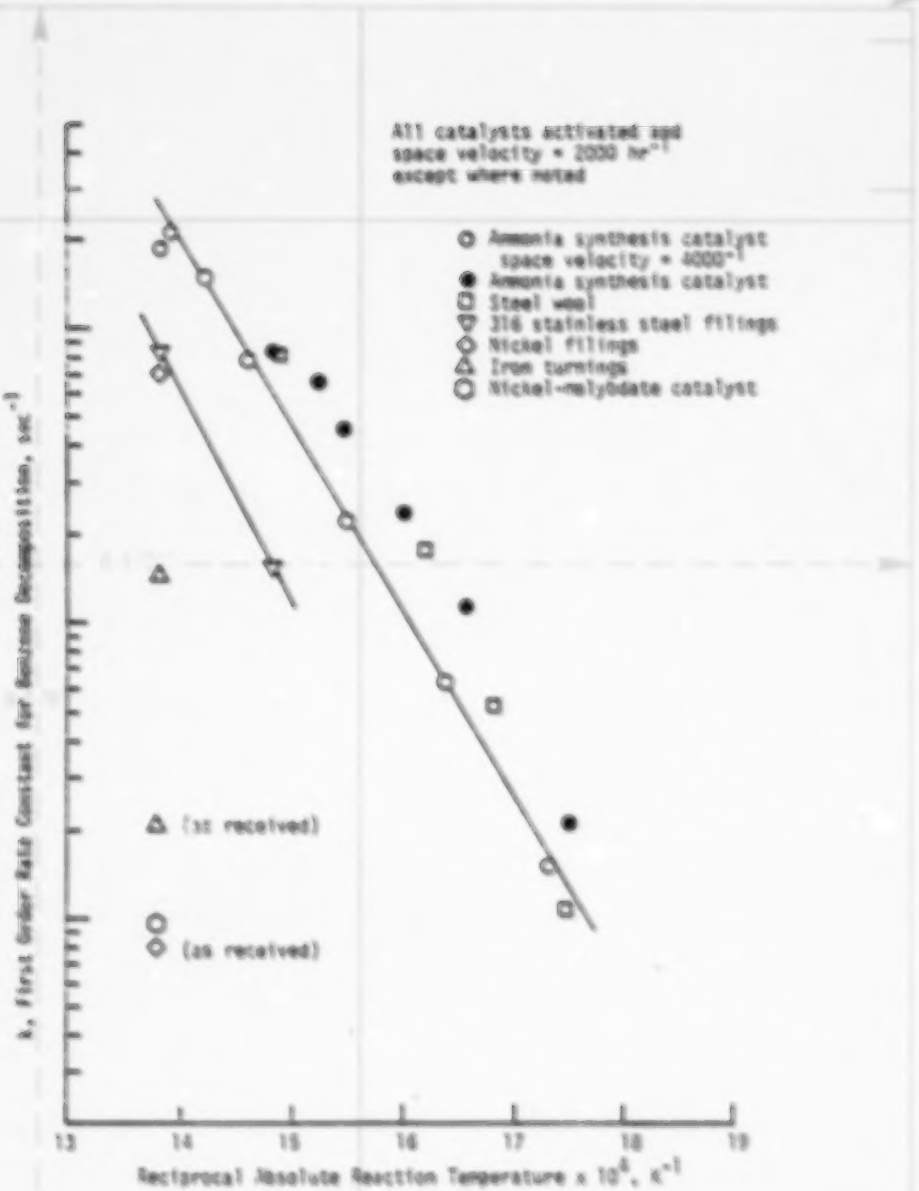

Figure 12. Rate constants for benzene hydrocracking over iron- and nickel-containing materials.

After 29 hr on stream, the rate constant leveled off to k = 3.33 sec^{-1}. This is in good agreement with the data for the ammonia catalyst taken at a space velocity of 4000 hr^{-1}, as can be seen in Figure 12. Another example where the activity decreased with time is the case where benzene-hydrogen-nitrogen mixture was passed over the NH_3 synthesis catalyst at 402°C and a space velocity of 4000 hr^{-1}. The activity of the catalyst went from k = 8.13 sec^{-1} initially to k = 6.06 sec^{-1} after 63 min on stream to a steady activity of k = 5.81 sec^{-1}. The initial activity of k = 8.13 sec^{-1} agrees with the data for a space velocity of 2000 hr^{-1} shown on Figure 12. Prior to this experiment at 402°C, the catalyst was tested at 432°C. During the tests at 432°C (and space velocity of 4000 hr^{-1}) the activity of the catalyst increased from k = 8.01 sec^{-1} initially to k = 13.9 sec^{-1} after 60 min on stream to a steady activity of k = 14.9 sec^{-1}. Prior to this test the catalyst was screened at 305°C. Based on these observations it appears that in a specific experiment with the ammonia synthesis catalyst the temperature of the previous experiment determines whether the activity of the catalyst increases or decreases with time on stream. If the previous experiment was performed at a lower temperature, the activity increases; on the other hand, if the previous experiment carried out was at a higher temperature, the activity decreases with time on stream. One mechanism which could explain this behavior is the deposition of carbon on the catalyst blocking active sites. Carbon could be removed from the surface by reaction with hydrogen; however, as the concentration of carbon on the surface decreases, the rate of this reaction would decrease until a dynamic equilibrium is established between the rate of deposition of carbon on the surface, and rate of removal by reaction with hydrogen.

In Figure 12, the least squares fit of the data is given for the 316 stainless packing at a space velocity of 2000 hr^{-1} and the ammonia synthesis catalyst at 4000 hr^{-1}. For the stainless steel the rate constant is given by $k = 1.23 \times 10^{11} \exp(-33{,}730/RT(°K))$ and for the ammonia catalyst $k = 1.60 \times 10^{10} \exp(-29{,}140/RT(°K))$. Referring to Table 2, it can be seen that the activation energy for the cracking of benzene on 316 stainless steel in the packed bed and the empty stainless steel reactor are close with the activation energy of the empty reactor being 36510 cal/gmol. By assuming that the activation energy for the reactor packed with 316 stainless steel is to be

the same as for the empty stainless steel reactor, the best fit of the data (Figure 12) for the packed reactor is $k = 8.57 \times 10^{11} \exp(-36{,}510/RT(°K))$. For the packed reactor the frequency is approximately 25,000 times that of the empty stainless steel reactor. This can be attributed to both the increase in material and surface area in the packed reactor and the oxidative pretreatment.

The effect of oxidative pretreatment on the activity of iron turnings and nickel filings is also shown in Figure 12. It can be seen that the peak activity of the iron turnings is approximately an order of magnitude greater after oxidation than before. The nickel filings showed approximately two orders of magnitude increase in the activity as a result of oxidation. However for both the iron turnings and nickel filings, the activity decreased rapidly from the peak to approximately the preoxidation activities of the respective materials.

Based on the screening study, the iron oxide catalyst and steel wool appeared to be the best materials for hydrocracking. It can be seen from Figure 12 that the nickel molybdate HDS catalyst is a poor catalyst for hydrocracking. This is to be expected since most HDS catalysts are formulated to prevent hydrocracking.

Following the screening study with benzene, the sulfur resistance of the various materials was tested. The activated materials were subjected to a thiophene-containing gas (50 percent H_2, 50 percent N_2, and 44 ppm thiophene) at a space velocity of 4000 hr^{-1}, 447°C, and approximately atmospheric pressure. The stainless steel, nickel filings, steel wool, and iron turnings showed virtually no resistance to thiophene poisoning with the hydrocracking activity decreasing to zero in a matter of minutes. The nickel molybdate HDS catalyst demonstrated complete conversion of thiophene to methane and hydrogen sulfide. The iron oxide NH_3 synthesis catalyst showed strong resistance to sulfur poisoning. This may be due to the alkaline promoters reacting preferentially with the sulfur. No sulfur was seen in the off-gas until 195 standard liters of the thiophene feed gas had passed through the reactor. The thiophene was initially completely converted to methane and the sulfur was chemisorbed. Approximately 3.55 cm^3 (standard) of thiophene per gram of synthesis catalyst was cracked prior to initial thiophene breakthrough.

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The benzene cracking activity of the ammonia synthesis catalyst was determined periodically as the catalyst was progressively poisoned by this thiophene reactant gas. This behavior is shown in Figure 13. In this figure the benzene cracking activity of the catalyst prior to thiophene breakthrough has been assumed to decrease linearly with the length of time that the thiophene reactant gas is on stream. The reason for this is that prior to breakthrough, the accumulation of sulfur in the catalyst bed is a constant and proportional to the rate of sulfur feed to the reactor. Assuming that the decrease in active sites for hydrocracking is proportional to the amount of sulfur absorbed, the rate of decrease in the benzene cracking activity should be a constant. After sulfur breakthrough, thiophene in the outlet of the microreactor was observed to slowly increase with time. In this case the rate of decrease in benzene hydrocracking activity would not be a constant but would decrease with time. Assuming that the rate of decrease in active sites is proportional to the number of active sites remaining in the catalyst, the rate constant for benzene hydrocracking should decrease exponentially with length of time that the thiophene reactant gas is passed through the catalyst bed. As shown in Figure 13 the data points, after breakthrough, are consistant with this mechanism, activity of the catalyst was determined after air oxidation and found to be $k = 0.677$ sec^{-1}. However, the benzene activity increased and leveled off after 19 hr on stream at $k = 1.71$ sec^{-1} which was the activity prior to air oxidation. Thus the regeneration was unsuccessful. The second attempt at regeneration was made on the catalyst after being exposed to the thiophene reactant gas for 128 hr. Conditions for the attempted regeneration was 650°C with air being passed over the catalyst for 2 hr at a space velocity of 2000 hr^{-1}. The benzene activity in this case was also approximately the same before and after oxidation indicating that the catalyst was not regenerated.

The regeneration temperatures of 450°C and 650°C that were chosen were based on the hypothesis that the sulfur in the catalyst was present as either ferric sulfide (FeS_2) or ferrous sulfide (FeS). Experiments on a thermogravimetric analyzer (TGA) showed that FeS_2 starts to lose weight in air at 450°C and the weight loss is nearly complete at 520°C. On the other hand, no appreciable weight loss for FeS is seen until 620°C. The loss is rapid from 620° to 690°C and then slows up until the maximum at 1200°C. It

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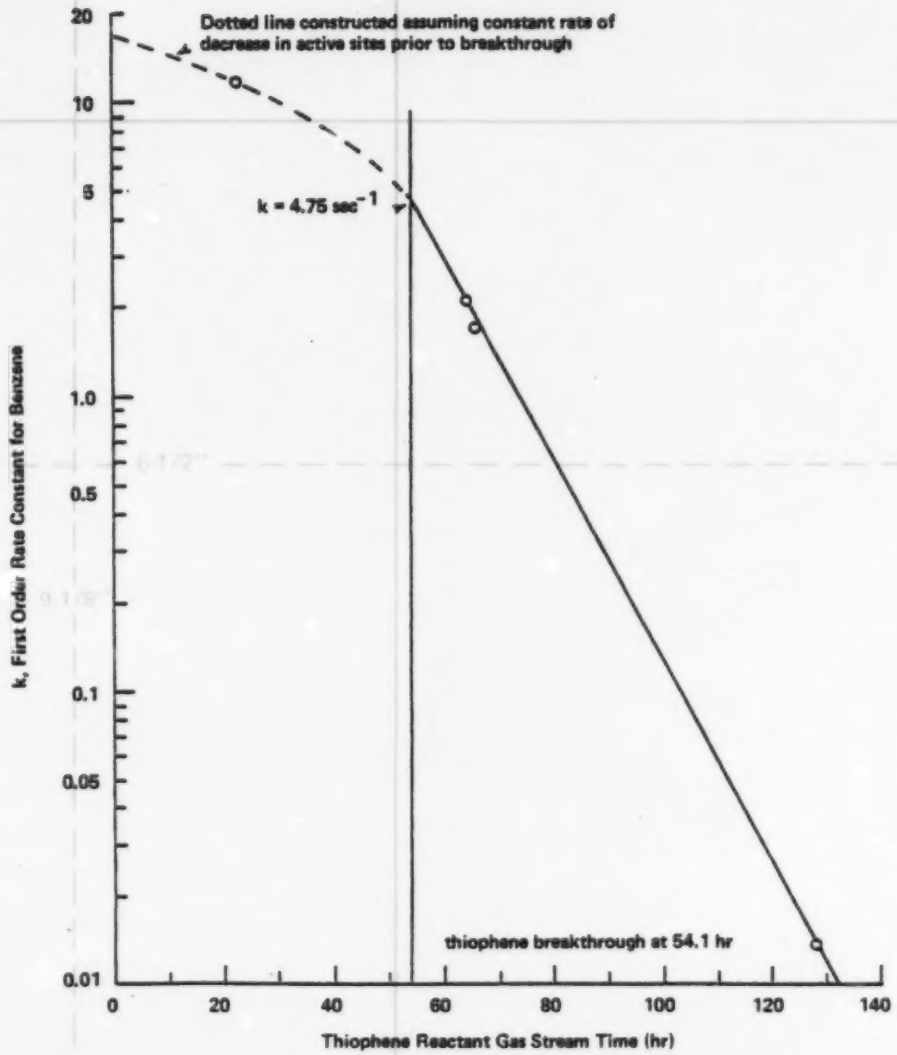

Figure 13. Benzene hydrocracking rate vs. thiophene reactant gas on stream time.

appears more likely that the sulfur is present in the poisoned catalyst as FeS than as FeS_2. However, the limited data on the TGA experiments and the microreactor catalyst regeneration experiments are not sufficient to confirm this theory.

Further studies are needed to define the procedures of reactivation. Air and/or steam treatment of the poisoned catalyst under controlled temperature conditions might be a possible approach. Furthermore, a need exists for defining the level of deactivation or sulfiding before reactivation should be carried out. Presumably a catalyst, which is about 50-70 percent deactivated, should be subjected to reactivation; i.e., the catalyst should not be allowed to deactivate completely. A need exists for further study of the iron oxide catalyst using the raw gas produced from coal gasification. This will be a true test of the feasibility of vapor phase cracking of pollutants produced from coal gasification. At this point the iron oxide catalyst looks quite promising for cracking of the pollutants. However, due to the presence of large amounts of sulfur in the raw gas, in addition to other impurities such as water vapor, ammonia, etc., this catalyst needs to be tested downstream of a coal gasifier so that feasibility of using this catalyst for pollutant control in coal gasification systems can be determined.

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SECTION 5

WET OXIDATION OF GASIFIER CONDENSATE

Wet oxidation has been under development for 30 years in the United States with specific applications toward the treatment of industrial wastes.[15,16,17] In 1976, there were more than 150 wet oxidation installations worldwide. Typically, the industrial wastes treated by wet oxidation are wastewaters containing such low levels of organic materials that the heat of combustion of the organics is not sufficient to vaporize the waste stream. Gasifier condensate is in this category of materials.

Gasifier condensate must be treated to reduce the organic content of the stream before it is reused in the gasification process. Typical commercial concepts for coal gasification processes call for stripping, solvent extraction, and biological oxidation of the condensate before being passed to the plant cooling water circuit. The use of wet oxidation to treat gasifier condensate may have several potential advantages over other processes:

1. According to C. F. Braun's studies (1) of gasification processes using eastern coal, the desirable level of steam in the feed to the shift converter is 40 percent. In order to maintain this level, the quench system must be operated at 210° to 230°C and 600 to 1000 psig. These are ideal conditions at which to sparge oxygen into the condensate and carry out wet oxidation of the organic material. Because the initial condensate temperature is high, expensive heat exchange equipment usually associated with wet oxidation may not be needed.
2. The condensate will contain suspended particles of gasifier char or ash. These particles contain minor and trace elements with (undetermined) potential to catalyze the oxidation reaction.
3. Medium- and high-Btu gasification processes include on-site oxygen

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generation capacity. Thus, treatment with oxygen (as opposed to air) may be feasible, permitting a reduction in the size of the treatment vessels.

4. Wet oxidation could reduce the levels of PNAs in the gasifier condensate which may be refractory to biological oxidation. If PNAs enter the biological oxidation units, the PNAs could accumulate in the sludge or be evolved into the atmosphere in the biological oxidation cell or cooling tower.

A simplified flow sheet for a unit, which could be used to carry out the wet oxidation of gasifier condensate, is shown in Figure 14. Condensate at 210° to 230°C is pumped to oxidation pressure and is preheated further in the heat exchange with the treated condensate. Oxygen is sparged into the reaction vessel where the organic content of the condensate is converted mainly to carbon dioxide and water. A gas-water mixture passes from the reactor to the separator where the gas and liquid products are separated. The exhaust gas will contain mainly carbon dioxide and some light hydrocarbons which are so volatile that they escape the reactor before being oxidized. The sulfur content of the condensate will be retained in the treated condensate as sulfates according to Pradt.[16]

A number of studies have been carried out on the wet oxidation of phenol in water. Studies concerning catalytic wet oxidation have been reviewed by Katzer et al.[18] and Bansal et al.[19] Katzer and coworkers have demonstrated that catalytic wet oxidation appears to be economically attractive as a treatment technique, compared with other available physical-chemical treatment techniques, for high to intermediate (>1000 ppm COD) concentrations of organics in wastewater streams. According to Forney,[20] gasifier condensate can have CODs up to 43,000 ppm. Thus, the condensate is likely a candidate for catalytic wet oxidation treatment.

One of the principal reasons for the research on catalysts for wet oxidation is to lower the temperature of the oxidation, and consequently reducing the degree to which heat integration must be carried out in the wet oxidation process in order to maintain high reaction temperatures. However, in high pressure gasification processes, the gasifier condensate will be available at 200°C or greater, and there may be a reduced need for the enhancement of oxidation rates by catalysts.

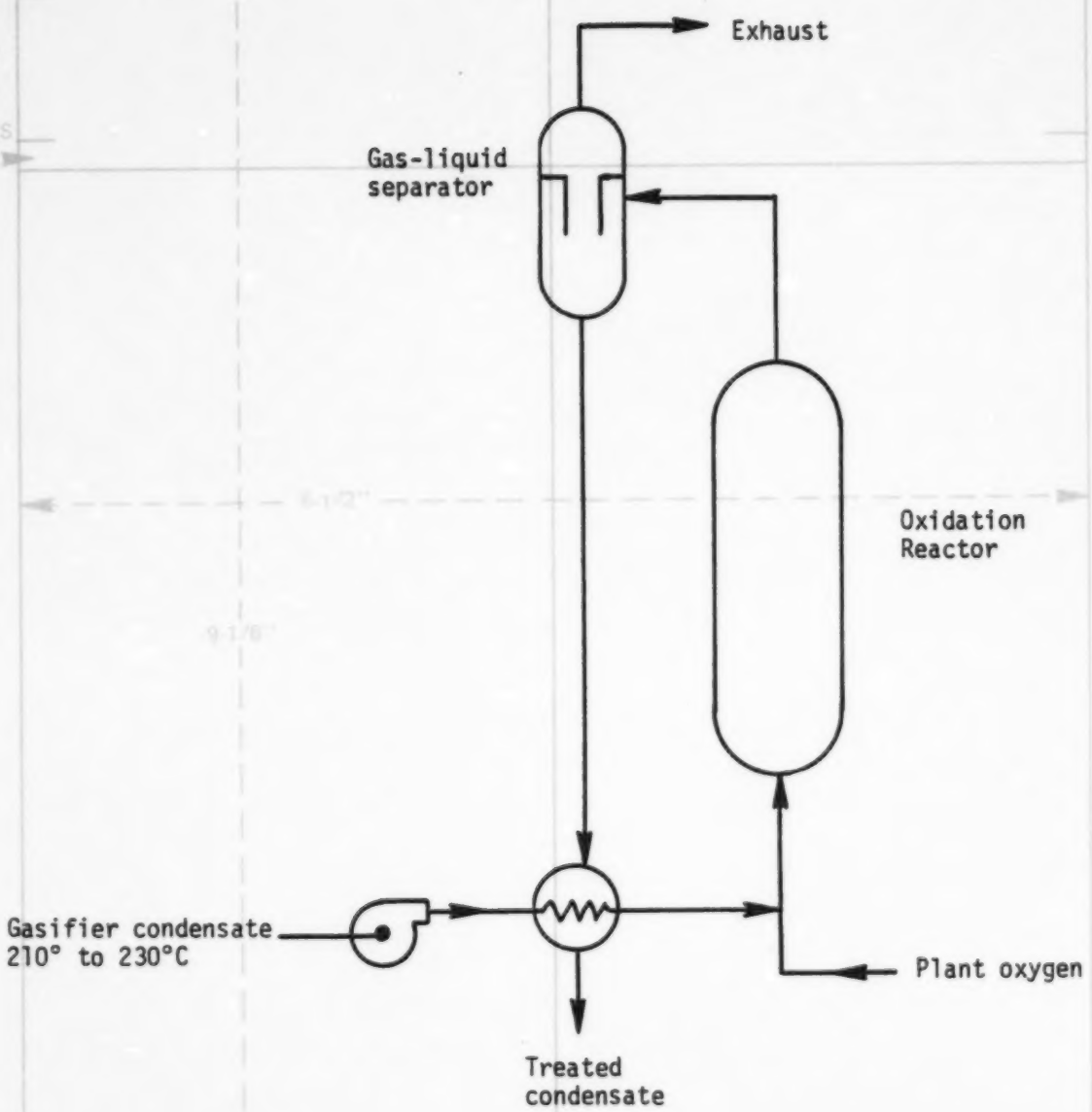

Figure 14. Simplified wet oxidation system.

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The purpose of RTI's research on wet oxidation was to determine whether reasonable rates of wet oxidation could be obtained with acutal gasifier condensate and whether gasifier ash or char could enhance the rate of wet oxidation.

EXPERIMENTAL

A simplified flow diagram for the system used for conducting wet oxidation experiments is shown in Figure 15. Material to be subjected to wet oxidation is pumped into a 1-liter autoclave using a Milton-Roy positive displacement metering pump. Oxygen of 99.5 percent purity, supplied from high-pressure gas cylinders, is sparged into the autoclave where the wet oxidation takes place. A back-pressure regulator downstream of the autoclave is used to control the system pressure. The product stream is cooled and the liquid product collected for chemical analysis. The flow rate of gases are monitored by a dry test meter.

The wet oxidation experiments have been conducted in a continuous feed, completely mixed, stirred tank mode. Liquid volume in the autoclave is determined by the height of the outlet tube above the bottom of the autoclave. The outlet tube is fitted with a sintered stainless steel frit which served to retain catalysts in the reactors.

Each wet oxidation test was started by bringing the autoclave to the desired temperature and pressure while adding oxygen and deionized water continuously. When the operating conditions were reached, the liquid feed was switched to gasifier wastewater or other feed material. At the initial liquid flowrate, 3 to 4 liquid space-times were permitted to elapse before sampling. The liquid flowrate, and thus the liquid space-time, was then changed. In this manner, at least three liquid samples were taken at varying liquid space-times. For those tests in which gasifier residue was used, the preweighed residue was added to the reactor before pressurization. Any adsorption of organics from solution upon these solid residues was expected to reach a steady-state long before any liquid samples are taken. Following each wet oxidation test, the reactor was cooled, depressurized, disassembled, and cleaned before the next test. The sample of the gasifier char retained in the reactor was saved for possible chemical analysis.

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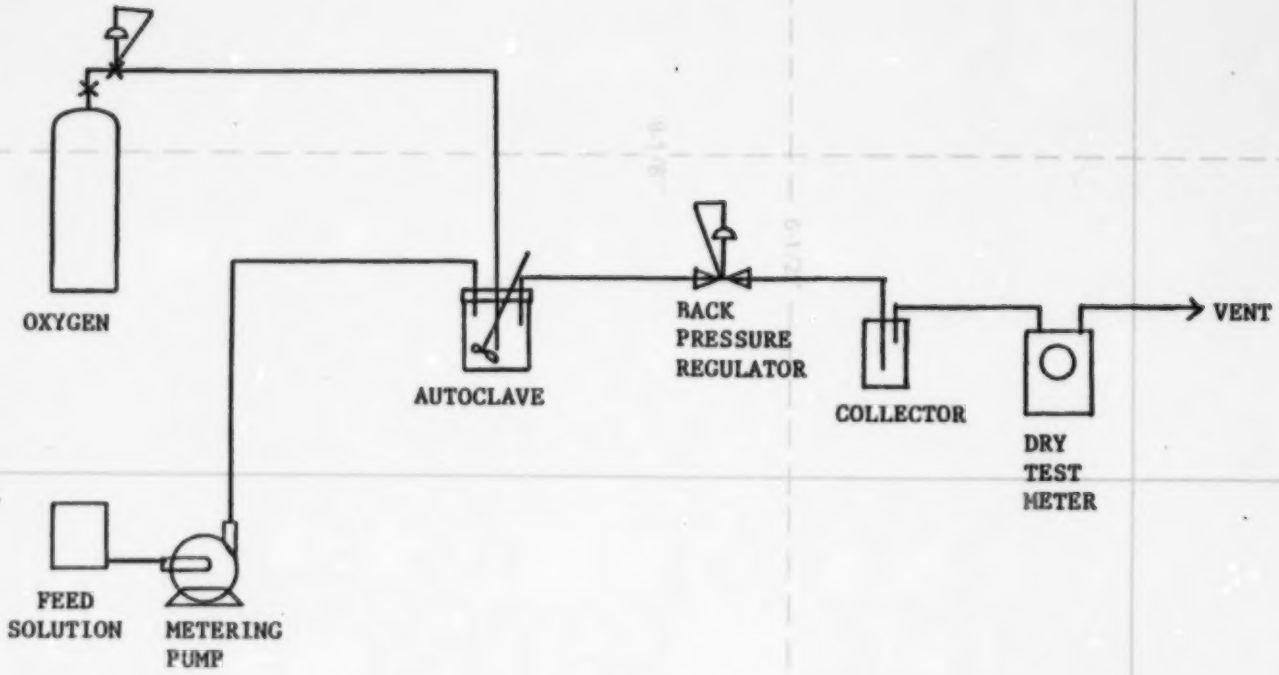

Figure 15. Autoclave/wet oxidation system.

RESULTS AND DISCUSSION

Six steady-flow wet oxidation tests have been performed. In four of these tests, the feed material was a solution of phenol (at approximately 10,000 ppm) in water; in the others, it was quench water produced in the North Carolina State University coal gasifier.[21] In three of the tests, sufficient Illinois No.6 bituminous coal char, which was produced in the RTI bench-scale gasifier, was added to the autoclave to bring the concentration of char in the autoclave to 5 g/l. An analysis of the char used is given in Table 6. In all tests the total system pressure was 500 psig.

Figure 16 summarizes the response of chemical oxygen demand (COD) of the two feed materials as a function of throughput (space-time), char loading, and temperature. Based on the data contained in this figure, it was found that no significant change in COD of the phenol solution occurres at a temperature of 150°C, even for very low throughputs (high space-times) and that at 200°C the COD of the phenol solution decreases rapidly with increase in space-time.

The data at 200°C have the appearance of a first-order decomposition of COD in a stirred tank reactor. This is a great simplification of the actual situation since COD is a measure of the total concentration of components which can be oxidized. However, under this simplification, COD in the outlet of the reactor as a function of space-time, τ, can be written

$$COD = \frac{(COD)_{inlet}}{1 + k\tau} \qquad (2)$$

where k = first-order rate constant. The curves shown in Figure 16 represent the least squares fit of the experimental data by this equation. For the case of wet oxidation of the phenol solution without char present, it was found that $k = 0.034\ min^{-1}$. The computation of the curve for these data excluded COD at 15 min. Including this point changes the curve only slightly and increased k to $0.040\ min^{-1}$. Addition of gasifier char to the reactor approximately doubled the rate of oxidation with the first-order rate constant being $0.073\ min^{-1}$.

Equation (2) was used to determine the rate constant for the wet oxidation of gasifier quench water without the addition of char to the reactor. The COD at a space-time of 48 min (see Figure 16) was not used in

TABLE 6 . ANALYSIS OF ILLINOIS NO.6 GASIFIER CHAR USED AS CATALYST IN WET OXIDATION TESTS

Proximate (%)	
moisture	0.77
ash	56.73
volatile matter	2.56
fixed carbon	39.94
Ultimate (%)	
moisture	0.77
ash	56.73
carbon	39.61
hydrogen	0.50
nitrogen	0.72
chlorine	0.06
(pyritic sulfur)	(0.06)
(organic sulfur)	(1.49)
(sulfate sulfur)	(0.01)
total sulfur	1.56
oxygen	0.05
Heating Value (Btu/lb)	6321
Trace Elements (μgram/gram)	
antimony	1.30
arsenic	21.2
bromine	<3.04
cadmium	<13.2
chromium	1620
mercury	<1.0
manganese	249.
nickel	826.
selenium	<2.71
zinc	<56.8
Size	
100% minus 50 mesh	

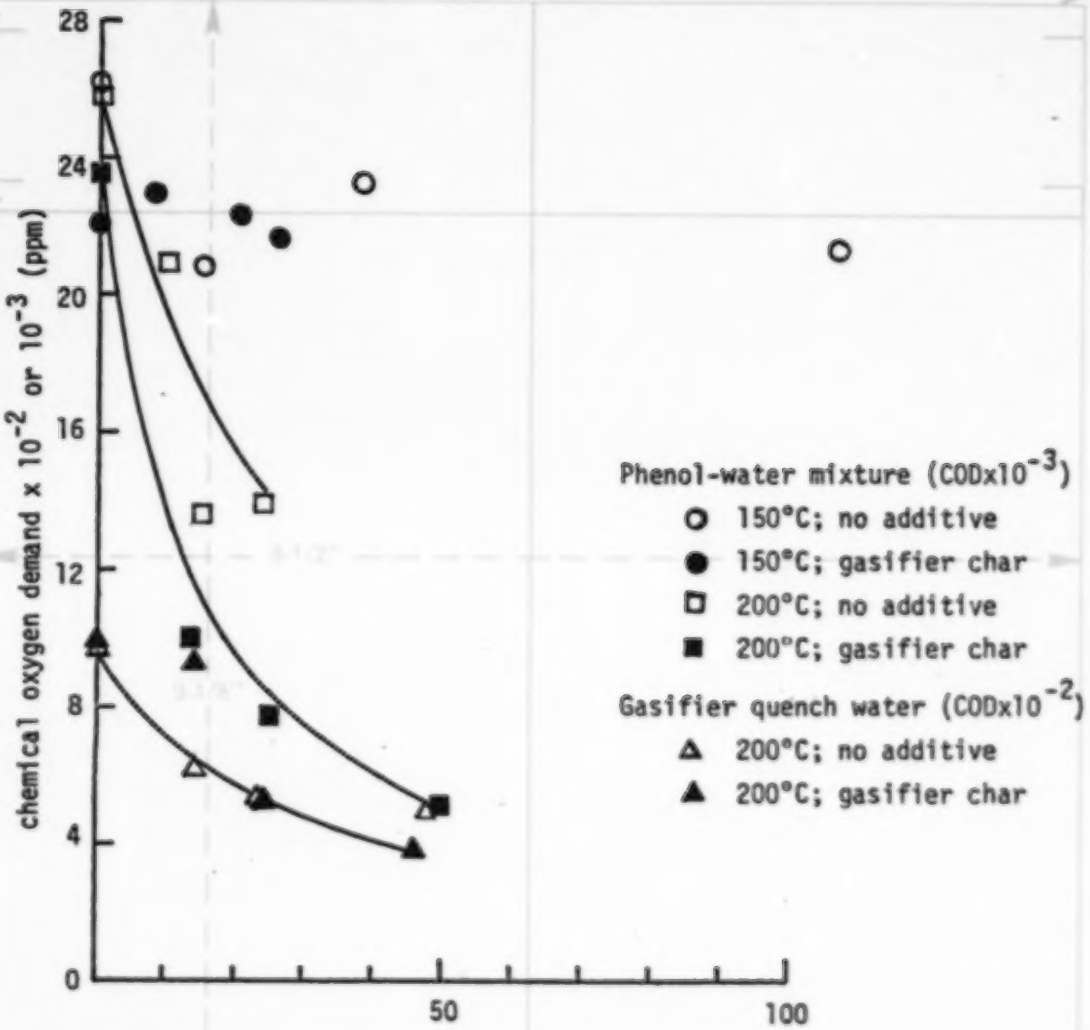

Figure 16. Wet oxidation test results.

the determination since it did not follow the trend of decreasing COD with space-time as observed for the phenol-water tests. The value of the rate constant was 0.036 min^{-1}. This is in good agreement with k = 0.034 to 0.040 min^{-1} computed for the oxidation of phenol in water. Addition of char to the reactor did not apparently increase the rate of oxidation of the organics in the quench water. In Figure 16, the curve passing through three of the data points for the oxidation of quench water in the presence of char is the same curve computed for the oxidation of quench water without char.

The rates of wet oxidation obtained in these experiments are comparable to those found in the literature for catalytic wet oxidation. Bansal et al.[19] reported data for phenol oxidation over a packed bed of copper chromite catalyst at 200°C. The rate constant they obtained would be equivalent to k = 0.012 min^{-1}. Katzer et al.[18] studied phenol oxidation over a copper oxide catalyst at 200°C in a stirred autoclave reactor. Analyzing their data and using Equation (2) yields a rate constant of k = 0.41 min^{-1}. Thus it can be seen, based on the conclusions of Katzer et al., that the wet oxidation rates obtained in the present experiments are in the range of economic interest.

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